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Paul Sharpe and Carolyn J. Cassady

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GAS-PHASE REACTIONS OF SILVER CLUSTER IONS PRODUCED BY FAST ATOM BOMBARDMENT

Paul SHARPE and Carolyn J. CASSADY

Department of Chemistry, Miami University, Oxford, OH 45056, USA

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Abstract

Silver cluster ions, Ag_x^+ (x = 1-16), have been produced by fast atom bombardment of silver foil and silver salts in the external ion source of a Fourier transform ion cyclotron resonance mass spectrometer. Ion formation and collision-induced dissociation are discussed in relation to ion stabilities. Reactions of Ag_x^+, x = 1-5, were studied with a variety of small molecules. Reactivity is dominated by adduct formation and silver atom displacement, which is dependent on cluster size. Contrasting reactivity was observed between Ag^+ and Ag_2^+ with 2-propanol, 2-methyl-2-propanol and 2-methylpropane.

1. Introduction

An understanding of the chemical behavior of microscopic metal surfaces is essential to the fields of catalysis and surface science. Information on structure and reactivity relationships of metal surfaces can be obtained from studies of gas-phase metal cluster ions. For example, the reactivity of metal clusters has been demonstrated to be a strong function of cluster size. [1-5] The reactivity of silver clusters is of considerable importance, since silver is used in catalytic oxidations [6] and the chemistry of silver clusters is the basis of photography [7].

Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR) [8] is a powerful technique for studying atomic metal ion and metal cluster ion chemistry. In addition to high mass accuracy and multistage MS capabilities, FT-ICR has the ability to trap ions and study their gas-phase ion/molecule reactions. Small metal cluster ions, including silver [9-11], have been generated by laser vaporization of metal-containing targets positioned within the high vacuum regions of FT-ICR systems. Larger metal cluster ions have been produced by coupling FT-ICR to ion sources located external to the analysis region. Although more elaborate, these techniques provide greater versatility and ready access to the cluster source. Smalley and co-workers have used FT-ICR to study large metal cluster ions generated in an external supersonic metal cluster beam source [12], while more recently, Irion and co-workers have coupled an external secondary ion source (Xe^+ SIMS) to FT-ICR [13]. Particle bombardment is an important alternative to laser vaporization for the production of metal cluster ions. For example, large silver cluster ions (Ag_x^+) of up to x = 250 have been reported in an

investigation of Xe^+ SIMS bombardment of silver foil. [14]

In the present study, silver cluster ions are generated by fast atom bombardment (FAB) of silver metal and silver salts in the external ion source of an FT-ICR. Collision induced dissociation (CID) and reactivity of small Ag_x^+, x = 1-5, is reported. The results provide new insights into the reactivity, stability and structure of silver cluster ions.

2. Experimental

All experiments were performed with a Bruker CMS 47X FT-ICR mass spectrometer, equipped with external ion source and 4.7 T superconducting magnet. [15] Silver cluster ions were generated by fast atom bombardment (FAB) on silver foil and pressed pellets of silver oxides and silver halides. Ions were produced in the external source using a Phrasor Scientific FAB gun [16] which employs an 8-10 kV beam of xenon atoms and ions with a bombarding particle density on the order of 10 μA cm^{-2}. Electrostatic focusing was used to transfer the ions from the source into the FT-ICR cell. Thermalization of the trapped ions was achieved by admitting a pulse of argon (2 x 10^{-5} mb) into the cell vacuum chamber immediately after ion transfer. A period of 1 second was allowed for collisional cooling and for the argon to be pumped away before monitoring ion/molecule reactions.

Silver bromide targets were used to generate Ag_x^+ clusters for ion/molecule reaction studies. Cluster ions were mass-selected by resonant frequency ejection techniques and allowed to react with static pressures of reactants in the range of (1-20)

x 10^{-7} mb. Reactions were monitored for times of up to 60 seconds.

Collision induced dissociation experiments were performed with xenon or argon collision gases at pressures in the range of (1-10) x 10^{-7} mb. The collision energy was varied from 0 to 150 eV (laboratory).

3. Results and Discussion

3.1. FAB Spectra of Silver Metal and Silver Salts.

Under our experimental conditions, FAB on silver foil produces pure metal cluster ions containing up to 16 atoms. The signal obtained from clean silver foil was relatively weak, and several thousand scans were required to obtain the spectrum shown in fig. 1. The distribution of cluster sizes displays the typical pattern observed in sputtering spectra of silver foil. [14] That is, greater abundance for odd atom clusters than for even, and the overall intensity decreasing with increasing cluster size. The greater stability of odd atom clusters has been attributed to their spin-paired electronic structure. [14]

The intensity of Ag_x^+ produced from FAB of silver salts was significantly enhanced over the ion intensity from silver foil. FAB of AgBr produced Ag_x^+ clusters with x = 1-9 and abundant silver bromide clusters $Ag_xBr_y^+$ (fig. 2), which have the stoichiometry $[Ag_x(AgBr)_y]^+$. The most abundant of these ions have x = 1, 3 and 5, which are also the most stable Ag_x^+ clusters. Low-energy CID experiments of several silver bromide clusters resulted in loss of AgBr units to yield the stable Ag_x^+ ion. Analogous ions are

observed in spectra produced by FAB of AgCl and AgI pellets. These silver halide cluster ions may be similar in structure to photographically developable microcrystals (latent image specks), which are composed of silver atom clusters on silver halide crystals. [7]

Silver oxide, AgO, produces Ag_x^+ clusters with x = 1-9 and $Ag_xO_y^+$, y = 1 and 2 (fig. 3). Similar spectra are obtained from FAB of Ag_2O and from silver foil pre-treated with 3M HCl. The silver oxide spectra also show variable abundances of species with a hydrogen atom incorporated into clusters with 2 and 4 silver atoms. For example, Ag_2H^+, $Ag_2HO_2^+$, Ag_2HO^+, Ag_4HO^+ and $Ag_4HO_2^+$ are observed in varying amounts, depending on the sample. Some of these species are prominent in fig. 3. The hydrogen atoms presumably originate from H_2O in the silver oxide lattices. Silver and hydrogen both have one valence electron. This suggests that the H atom in these clusters is bound to the silver atoms to form species isoelectronic and probably isostructural with the more stable odd atom clusters. A similar effect has also been observed for copper cluster ions.[17] The effect is not seen with Ag_6^+ or higher even atom clusters, probably because the difference in stability between adjacent clusters is too small.

3.2. Collision-Induced Dissociation and Reactions of Ag_x^+.

Low-energy CID experiments were performed to investigate the stability of Ag_x^+ clusters for x = 2-5. Both Ag_4^+ and Ag_5^+ readily dissociate to yield Ag_3^+, while Ag_2^+ readily dissociates to Ag^+. Dissociation of Ag_3^+ requires relatively high collision energies in excess of 100 eV (laboratory), which produces Ag^+ with minor amounts of

Ag_2^+. The special stability of Ag_3^+ has also been noted in CID studies by Freiser and co-workers [11], and Ag_3^+ is predicted by electronic considerations to be a highly stable ("magic number") cluster [14]. Higher energy collisions of Ag_x^+ (x = 2-5) yield Ag^+ for all cluster ions.

Reactions of Ag_x^+ were investigated with a variety of small molecules. No reactions were observed with oxygen, deuterium, methane, ethane, propane, butane, water, methanol and ethanol. The predominant pathway with other reactants is adduct formation,

$$Ag_x^+ \ (x = 1,3,4,5) \ + \ L \ \rightarrow \ Ag_xL^+. \qquad (1)$$

The Ag_xL^+ product ions undergo further ligand addition leading to the formation of $Ag_xL_y^+$. The terminal products of this adduct formation are given in Table 1.

All reactions of Ag_2^+, and some with Ag_4^+, involve initial addition of a reactant molecule with displacement of a silver atom to form AgL^+ and Ag_3L^+ respectively,

$$Ag_x^+ \ (x = 2,4) \ + \ L \ \rightarrow \ Ag_{(x-1)}L^+ \ + \ Ag. \qquad (2)$$

These primary product ions then undergo further addition of L to produce $Ag_{(x-1)}L_y^+$. CID studies of AgL_y^+ produce Ag^+, indicating that intact L ligands are bound to Ag^+. The bond dissociation enthalpy in Ag_2^+ is reported to be 38.3 ± 1.2 kcal mol^{-1}. [18] Assuming ΔS° for reaction 2 is zero, the displacement of Ag from Ag_2^+ by the molecules listed in Table 1 indicates that the resulting AgL^+ have Ag^+-L bond

dissociation enthalpies in excess of 38.3 kcal mol^{-1}.

Signal intensities of Ag^+ and Ag_3^+ were strong, permitting sufficiently long reaction times to observe the maximum value for y in AgL_y^+ and $Ag_3L_y^+$ (Table 1). That is, a clear kinetic barrier had been reached to any further addition of L molecules. Ion intensities of Ag_4^+ and Ag_5^+ were weaker, and addition reactions could not be monitored to completion.

Theoretical studies have predicted that Ag_3^+ exists with high stability in a triangular geometry. [19,20] Addition of reactant molecules to Ag_3^+ consistently produces $Ag_3L_3^+$ as a terminal product (Table 1), and each stepwise reaction occurs at comparable rates even for bulky molecules such as 2-methyl-2-propanol and benzene. Steric requirements for such barrierless additions suggest that the most probable structure for $Ag_3L_3^+$ is triangular with one molecule attached to each silver atom. Assuming the electronic structure of Ag_3^+ is not significantly perturbed by the addition of ligands, this is consistent with a triangularstructure for Ag_3^+. In addition, our ion formation and CID experiments also suggest a highly stable Ag_3^+ structure.

Rates of all addition reactions are slow compared to collision rates. Bimolecular rate constants for adduct formation, reaction (1), are in the range of (1-4) x 10^{-11} cm^3 $molecule^{-1}$ sec^{-1}. The low pressures used in FT-ICR do not provide efficient third body stabilization of adduct ions, which undergo unimolecular back-dissociation. This is probably responsible for the failure to observe adduct formation with smaller molecules such as water and methanol, rather than thermodynamic considerations. A similar effect has been noted in the reactivity of CO with metal cluster ions. [3] The rate of formation of AgL^+ from reactions with Ag_2^+ was approximately an order of magnitude

faster than from Ag^+. With Ag_2^+, the initial collision complex eliminates a silver atom, stabilizing the resulting ion AgL^+.

3.3. Organic Bond Cleavage Reactions of Ag_x^+.

For the majority of the reactions investigated, the Ag_x^+ clusters, x = 1-5, do not cause bond cleavage in reactant molecules. However, Ag^+ and Ag_2^+ display distinct reactivity with 2-propanol, 2-methyl-2-propanol and 2-methylpropane invclving bond cleavage. Reaction of 2-propanol with Ag^+ results in dehydrogenation,

$$Ag^+ + CH_3CH(CH_3)OH \rightarrow Ag(C_3H_6O)^+ + H_2. \quad (3)$$

Dehydrogenation does not occur with Ag_2^+, instead 2-propanol displaces a Ag atom,

$$Ag_2^+ + CH_3CH(CH_3)OH \rightarrow Ag(CH_3CH(CH_3)OH)^+ + Ag. \quad (4)$$

In contrast, Ag^+ dehydrates 2-methyl-2-propanol

$$Ag^+ + (CH_3)_3COH \rightarrow Ag(C_4H_8)^+ + H_2O, \quad (5)$$

whereas Ag_2^+ undergoes silver atom displacement,

$$Ag_2^+ + (CH_3)_3COH \rightarrow Ag((CH_3)_3COH)^+ + Ag \quad (6)$$

Low-energy CID of $Ag((CH_3)_3COH)^+$ formed by reaction (6) gave only Ag^+ as a product ion indicating an intact $(CH_3)_3COH$ ligand bound to Ag^+. This suggests that Ag^+ cannot cleave the C-C bonds of 2-methyl-2-propanol. In addition, to silver atom displacement, formation of $Ag(C_3H_5)^+$ is observed as a minor pathway in the reaction of Ag_2^+ with 2-methylpropane,

$$Ag_2^+ + (CH_3)_3CH \rightarrow Ag(C_3H_5)^+ + (AgCH_5) \quad (7)$$

but no reaction at all is observed with Ag^+. Only ionic products are detected in FT-ICR and the neutral species produced in reaction (7) are unknown. In $Ag(C_3H_5)^+$, C_3H_5 is probably bound as an intact η^3-allyl ligand, because our results indicate that Ag^+ is not facile at C-C bond cleavage. The reaction pathways of Ag^+ and alcohols are in agreement with previous investigations [21-23].

4. Conclusions

The present investigation has demonstrated that Ag_X^+ can be produced by FAB of silver metal and silver salts. The greater stability of odd atom clusters than even atom clusters was reflected in mass spectra and in CID experiments. Reactivity also varied with cluster size. Ag_3^+ and Ag_5^+ formed adducts with reactant molecules, while silver atom displacement reactions were observed in the reactions of Ag_2^+ and Ag_4^+.

Formation of $Ag_3L_3^+$ and the high stability of Ag_3^+ observed in CID experiments provides evidence supporting the theoretical triangular structure of Ag_3^+. We are presently expanding these investigations to include larger molecules and other group 11 metal cluster ions.

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Table 1. Terminal Products Observed in the Reactions of Ag_x^+ with Small XMolecules.

Reactant (L)	Ag^+	Ag_2^+	Ag_3^+	Ag_4^+	Ag_5^+
Ethene	AgL_4^+	NR[a]	$Ag_3L_6^+$	NR	NR
Propene	AgL_2^+	AgL_2^+	$Ag_3L_3^+$	NR	NR
1-Butene	AgL_2^+	AgL_2^+	$Ag_3L_3^+$	Ag_4L^+	NR
Cis-2-Butene	AgL_2^+	AgL_2^+	$Ag_3L_3^+$	Ag_4L^+	NR
Benzene	AgL_2^+	AgL_2^+	$Ag_3L_3^+$	Ag_3L^+	$Ag_5L_2^+$
1-Propanol	AgL_2^+	AgL_2^+	$Ag_3L_3^+$	Ag_3L^+	$Ag_5L_2^+$
2-Propanol	AgL_2^+	AgL_2^+	$Ag_3L_3^+$	Ag_3L^+	$Ag_5L_2^+$
2-Methyl-2-Propanol	AgL_2^+	AgL_2^+	$Ag_3L_3^+$	Ag_3L^+	$Ag_5L_3^+$
Acetone	AgL_2^+	AgL_2^+	$Ag_3L_3^+$	Ag_3L^+	$Ag_5L_2^+$
Ammonia	AgL_2^+	AgL_2^+	NR	NR	NR
Acetonitrile	AgL_3^+	AgL_3^+	$Ag_3L_3^+$	NR	NR

[a]NR indicates no observed reaction under our experimental conditions.

Figure Captions

Fig. 1. FAB mass spectrum of Ag foil obtained by signal averaging of 5000 scans.

Fig. 2. FAB mass spectrum of AgBr obtained by signal averaging 200 scans.

Fig. 3. FAB mass spectrum of AgO obtained by signal averaging 200 scans.

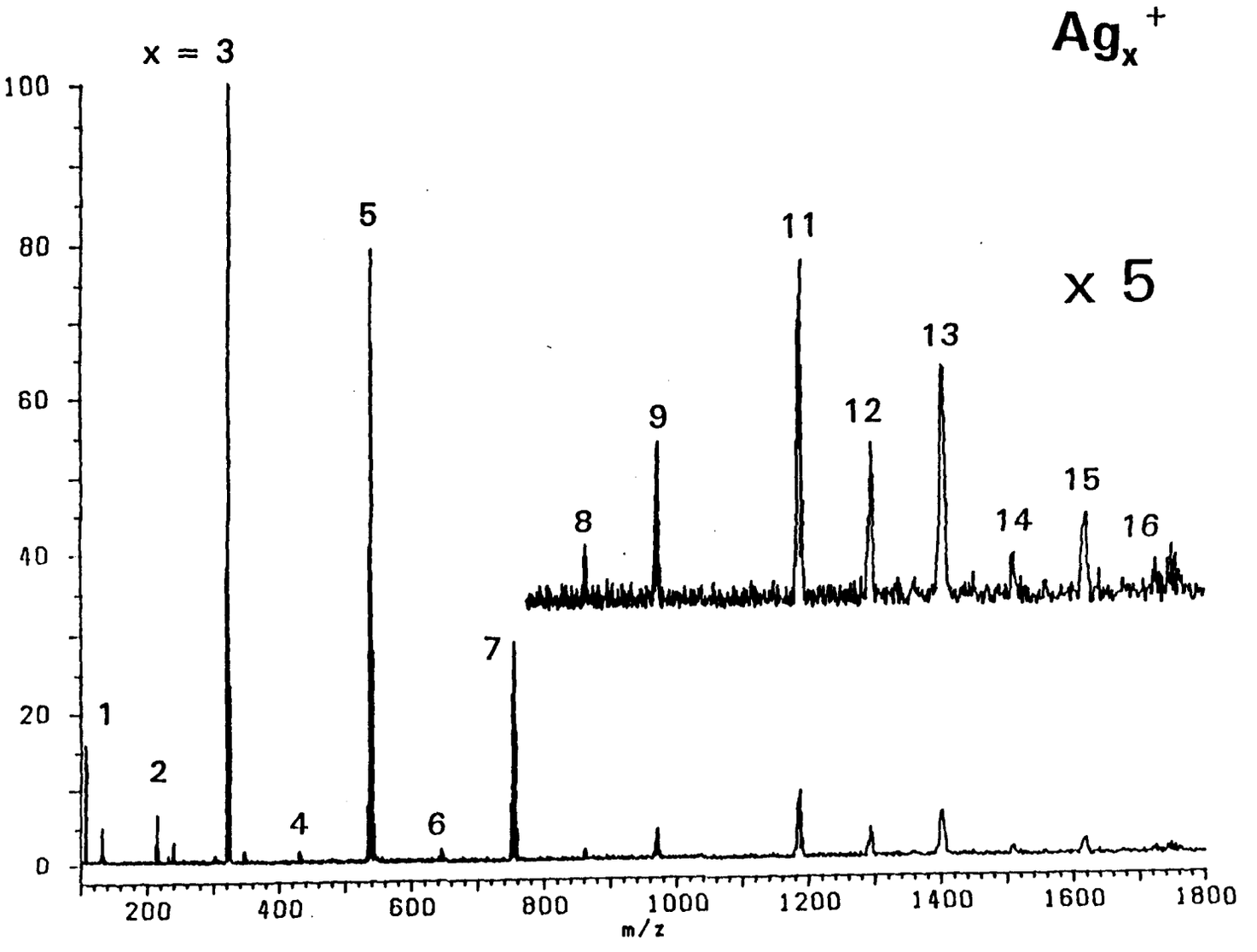
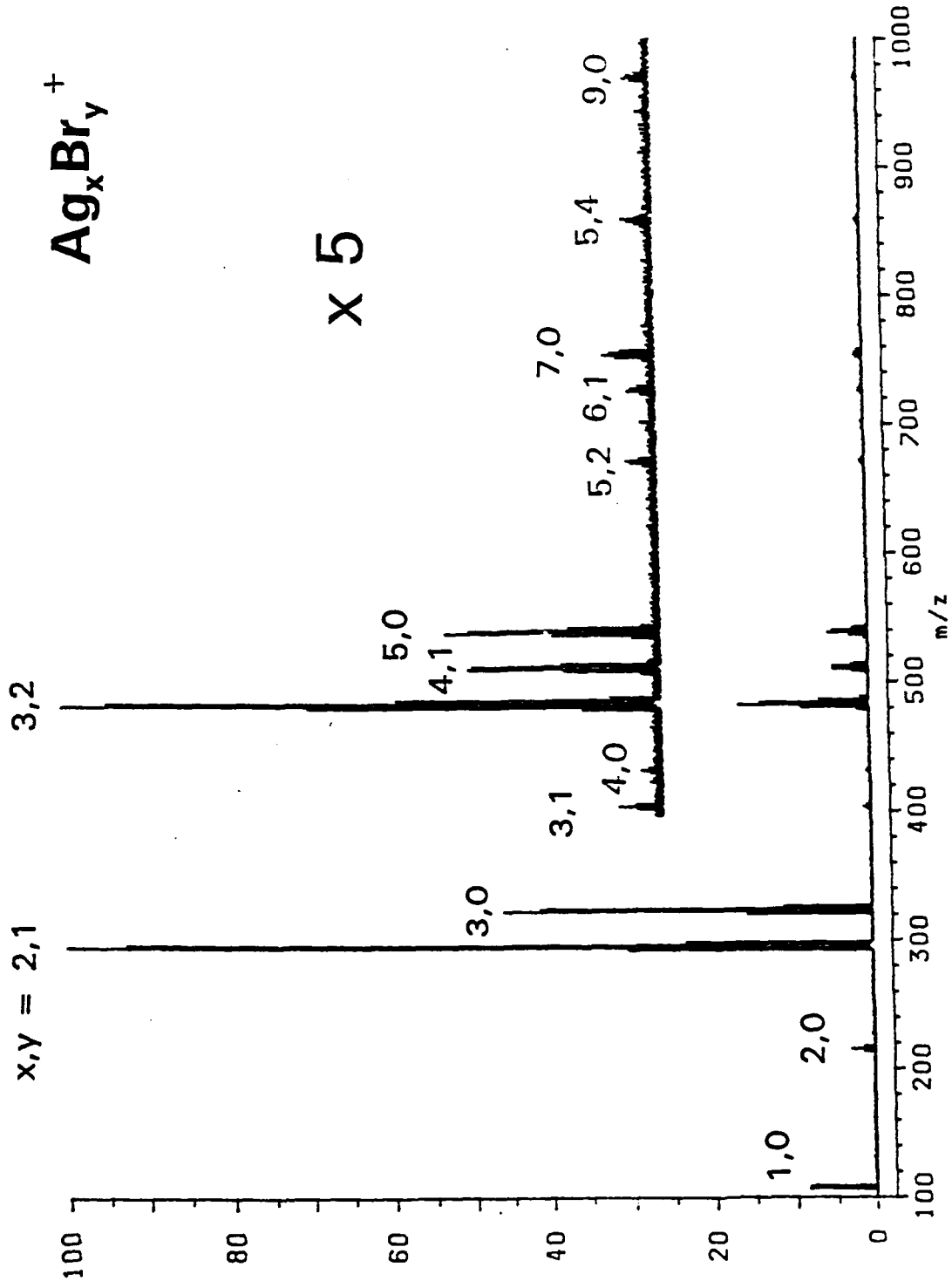

Ag_x^+
x = 3
x 5
100
80
60
40
20
0
200
400
600
800
1000
1200
1400
1600
1800
m/z
1
2
4
5
6
7
8
9
11
12
13
14
15
16

Figure 1

Figure 2


$Ag_xBr_y^+$
x,y = 2,1
x 5
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2,0
3,0
3,1
3,2
4,0
4,1
5,0
5,2
6,1
7,0
5,4
9,0
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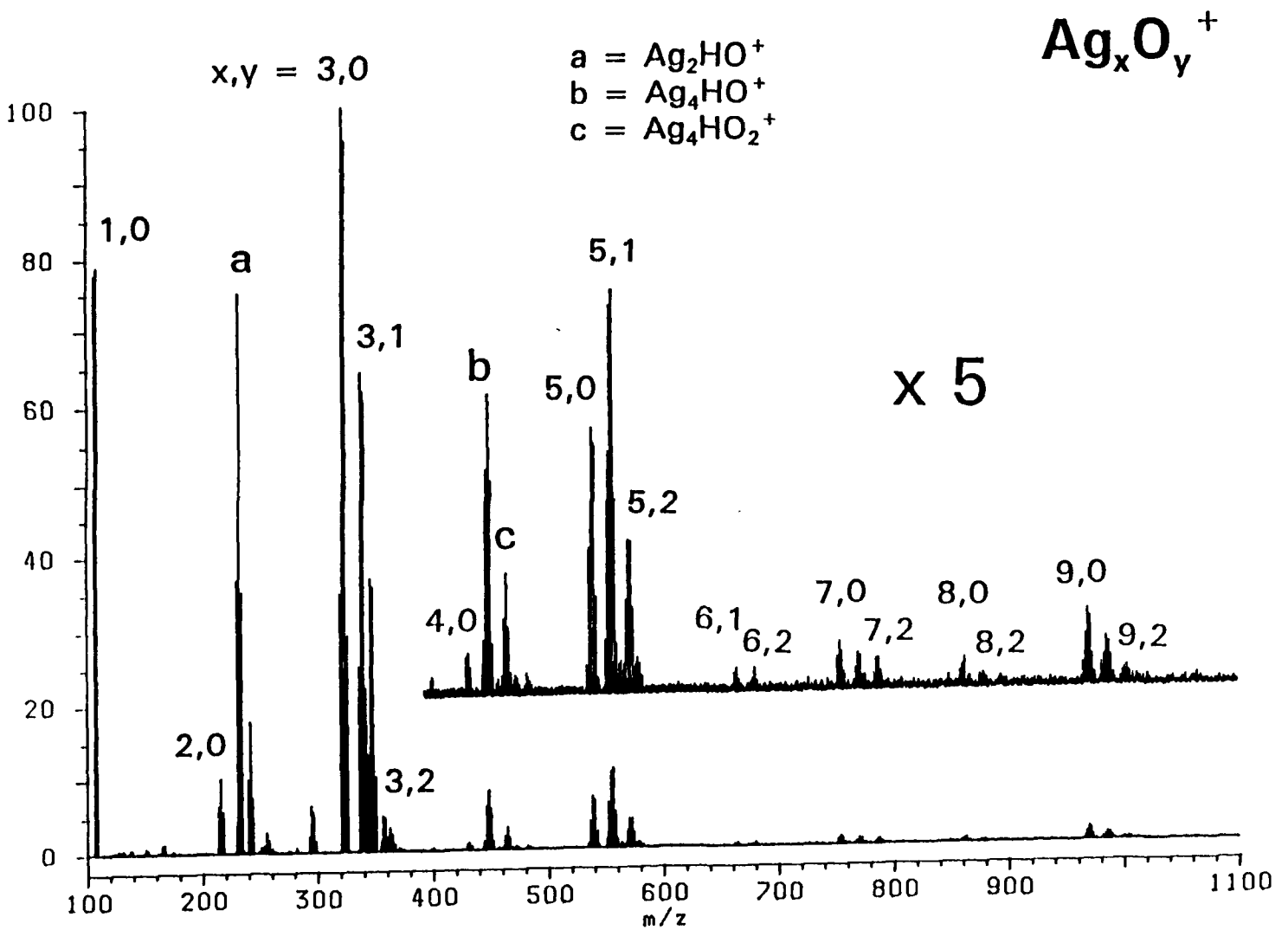
40
20
0
100
200
300
400
500
600
700
800
900
1000
m/z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a = Ag2HO+
b = Ag4HO+
c = Ag4HO2+
AgxOy+
x 5
1,0
a
3,1
b
5,0
5,1
c
5,2
4,0
6,1
6,2
7,0
7,2
8,0
8,2
9,0
9,2
2,0
3,2
100
80
60
40
20
0
100
200
300
400
500
600
700
800
900
1100
m/z

Figure 3

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